

Favorable reconsideration and withdrawal are also requested of the rejections of claims 1-6, 8-10 and 16 as being anticipated by, and of claim 7 as being obvious over, U.S. patent 6,729,248 to Johnson et al., which has been assigned to ADA Environmental Solutions, LLC. The Johnson et al. patent, however, issued from an application filed AFTER the effective filing date of the subject patent application (January 11, 2001) and so is not prior art. The Johnson et al. patent claims priority to a provisional application filed on June 26, 2000, which is about seven months before the effective filing date of the subject patent application, however the provisional patent application does not support the claims of the Johnson et al. patent, nor does it disclose or render obvious any of the subject claims. A copy of the Johnson et al. provisional patent application is enclosed for easy reference. It will be noted that the provisional application, for example, does not disclose or suggest a composition that is free of an added fluxing agent. In fact, it states that the composition comprises 2% to 8% zinc and requires at least 0.5% zinc. Moreover, it states that further experimentation is ongoing and betrays no recognition of the possibility of a composition free of a fluxing agent. Thus, it is clear that Johnson et al. did not have possession of the invention as of the filing date of their provisional patent application. Accordingly, neither the Johnson et al. patent nor the provisional application render any of the subject claims unpatentable.

Favorable reconsideration is further requested of the rejection of claims 1-10 as being obvious over the Buecker et al. article. That article is dated November 2000, which is less than a year prior to the effective filing date of the subject patent application and so is not prior art. Regardless, the article reports on a method of ADA Environmental Solutions, which appears to be the method of the Johnson et al. patent discussed above, which was assigned to ADA Environmental Solutions. Thus, even were the Buecker et al. article prior art, the subject claims

still are patentable over the Buecker et al. article for at least the reasons addressed above with respect to the Johnson et al. patent, including the fact that the Johnson et al. methods employed compositions that included an added fluxing agent (zinc). In fact, the Buecker et al. article explicitly notes that the ADA compositions included “a mixture of iron oxides and stabilizing chemicals . . .” See page 2 of 4, last full paragraph, of the Beucker et al. print-out. Accordingly, the Buecker et al. article does not render any of the subject claims unpatentable.

Finally, favorable reconsideration and withdrawal are also requested of the rejection of claims 1-10 and 16 as being obvious over the Radway patent. It appears from the rejection that the Examiner may not have seen applicant’s preliminary remarks addressing that patent, which answer the concerns raised by the Examiner. Thus, the preliminary remarks are repeated here.

U.S. patent 5,819,672 to Radway et al. had been cited in the prosecution of the parent application. Pending claims 1-10 and 16 in the subject application define patentably over the Radway et al. patent. Claim 1 calls for a method for increasing efficiency of heat transfer of a furnace in which calcium-containing coal is burned. The method comprises (a) adding to the coal enough of a fluxing agent-free composition comprising an iron compound to produce treated coal that is free of added fluxing agent and contains an effective amount of the iron compound; and (b) burning the treated coal, forming calcium ferrite, thereby increasing the efficiency of the heat transfer of the furnace. This method differs from that disclosed by Radway et al.

The method of the Radway et al. patent, as described in the patent’s specification, defined in the patent’s claims and illustrated in the patent’s working examples, is the standard prior art technique over which the present invention provides an improvement –it is the coating of furnace wall ash with a darkening agent. For example, the Radway et al. Abstract states, “The method

involves exposing the walls to a darkening agent, or a combination of a darkening agent and a fluxing agent.” And, again, in the Field of the Invention, Radway et al. state that “the invention relates to a darkening agent for darkening highly reflective deposits of thin ash . . .” And, again, in the Summary of the Invention, Radway et al. state, “The method involves exposing the walls to a darkening agent, or a combination of a darkening agent and a fluxing agent.”

Although Radway et al., in passing, mention that the darkening agent alone may be used to darken the ash, the examples only teach the use of the darkening agent with a fluxing agent. The fluxing agent allows the darkening agent to adhere to the ash. By contrast, the method of the present invention does not involve exposing the furnace walls to a darkening agent and a fluxing agent. Moreover, although Applicant argued in Preliminary Remarks A that the present invention inhibits the accumulation of ash on the wall, with additional research data, Applicant has discovered that the invented fluxing agent-free composition might not reduce total ash accumulation (although it is still believed that the amount of reflective ash is reduced), but has confirmed that, as noted in the subject specifications the composition increases the efficiency of heat transfer of the furnace. The composition appears to increase such efficiency by increasing the thermal conductivity of the ash on the furnace walls. Radway et al. further do not teach or suggest formation of calcium ferrite. The Radway et al. patent is directed consistently and single-mindedly to coating reflective ash build-up with a darkening agent and a fluxing agent.

Nor do Radway et al. provide any hint as to how to carry out its method (e.g., with respect to concentrations, type of iron ore, and techniques), let alone the claimed method. Radway et al. simply did not appreciate that if iron oxide were added to the coal in the proper amount, it would form calcium ferrite upon combustion of the coal, thereby obviating the need to

coat white ash as it directs, and nothing in the Radway et al. patent so teaches or suggests. This surprising result is sufficient to establish patentability.

CONCLUSION

In view of the foregoing, favorable consideration and early allowance of claims 1-10 and 16 are earnestly solicited.

Respectfully submitted,



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Attachments

06/26/00
U.S. PTO
100-895



is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)(2).

100-406 U.S. PTO
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TITLE OF THE INVENTION (280 characters max)

"LOW-COST TECHNOLOGY TO IMPROVE OPERATION OF CYCLONE FURNACES FIRING LOW-SULFUR WESTERN COALS"

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ENCLOSED APPLICATION PARTS (check all that apply)

X	Specification	Number of Pages	7	Small Entity Statement
X	Drawing(s)	Number of Sheets	0	Other (specify)

METHOD OF PAYMENT (check all that apply)

X	A check or money order is enclosed to cover the filing fees	19-1970	PROVISIONAL FILING FEE AMOUNT (\$)	\$150.00
X	The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number:			

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

No.

Yes, the name of the U.S. Government agency and the Government contract number are: _____

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TYPED OR PRINTED NAME: Christine Jacquet

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Low-cost Technology to Improve Operation of Cyclone Furnaces Firing Low-Sulfur Western Coals

Abstract

The present invention discloses a process to enhance the operational performance and cost-effectiveness of cyclone furnaces firing low-sulfur Western coals by adding to the fuel quantities of low-cost, iron-bearing materials produced as a byproduct of iron and steel manufacturing. Cyclone furnaces are designed to collect and discharge ash from the coal as a molten liquid known as slag. In order to melt into a slag at normal combustion temperatures (2600-3000 F), cyclone furnaces are designed to burn coals whose ash contains high amounts of iron and low concentrations of alkali and alkaline earth metals. The iron both reduces the melting temperature of the ash, and increases the slag viscosity at these temperatures due to the presence of iron aluminosilicate crystals in the melt. When low-sulfur western coals, with low iron and high calcium contents, are fired in these boilers, the viscosity of the slag is not in the proper range to provide satisfactory operation of the furnace and results in poor combustion. To overcome these slagging problems, utilities must crush the coal to a smaller size, blend in high-iron coal or add iron pellets (iron filings, scrap iron, or iron ore have also been used), all of which greatly increase operating and maintenance costs.

The use of inexpensive iron-bearing byproduct material is a novel means to provide a less costly fix to this problem. In addition to being less expensive, the physical characteristics of these materials provide additional benefits that potentially make them more effective than the other sources of iron. However, to provide an effective system for enhancing combustion in cyclone furnaces, there are several key steps in this process including proper selection of candidate material, treatment of the dust to allow handling and shipping, blending with the coal, and control of the feedrate.

Field of Invention

This process is applicable for use in the coal-fired electric utility industry. It is specifically of use for utilities that employ cyclone furnaces to fire low iron, high-alkali coals such as those found in the western regions of the United States. The invention may also be extended by those skilled in the art to apply to any industrial boiler that produces a molten, liquid ash residue (known to the industry as "wet-bottom" boilers).

Background of Invention

Cyclone furnaces are used to generate steam for power production and industrial processes. Such a furnace is diagrammed in figure 1. The furnaces operate by maintaining a sticky layer of fluid ash (slag) on the inside walls of the cyclone combustor. Coal is crushed to a 1/4-inch top size and blown into the burner end of the cyclone combustor. The whirling motion of the combustion air (hence the name "cyclone") propels the coal toward the furnace walls where the coal is caught like flies in flypaper and burns in the slag. Products of combustion exit the cyclone through an opening called the re-entrant throat at the opposite end from where the coal was introduced. Molten slag flows slowly through a spout to a hole in the bottom of the boiler where it is water-quenched and recovered as a saleable byproduct. The ash composition is critical to prevent the slag from freezing in the hole and causing pluggage. Therefore, cyclone furnaces were located in the mid-west to burn local high-sulfur, high-iron coals. Over time, cyclone furnaces have been converted to burn low-sulfur coal to satisfy environmental regulations limiting SO₂ emissions.

When certain high-calcium, low-sulfur coals from the Powder River Basin of Montana and Wyoming are burned in these furnaces, the cyclones do not develop a thick enough layer of sticky slag and the coal is not caught. This poor slag coating leads to unburned coal, degraded performance of particulate collectors (leading to stack opacity violations), and increased fuel and maintenance costs. The sticky slag layer can be reestablished by increasing the iron content of the coal.

It has been known for many years that iron is an effective fluxing agent for certain alumino-silicate glasses. Iron oxide fluxes high-silica glass, while reduced forms of iron (FeO or Fe-metal) flux calcium-rich glass. In the presence of burning coal particles, iron exists primarily in reduced form. Its use has been recommended to solve slag-tapping problems in cyclone furnaces by either blending in high iron coal or adding commercially available iron pellets, both of which are very expensive. The pellets (due to their size) have a further disadvantage of forming pools of reduced iron that can be very corrosive to metal or refractory surfaces exposed to it. Therefore, iron fluxes have never achieved long term acceptance in the utility industry.

The use of inexpensive iron-bearing byproduct material is a novel means to provide a less costly and technically superior fix to this problem. In addition to being less expensive, the physical characteristics of these materials provide additional benefits that potentially make them more effective fluxes than commercially available sources of iron.

Summary of Invention

It is the object of the present invention to improve the performance of cyclone furnaces burning low-iron, high-alkali coals by enhancing the slagging characteristics of the ash through the addition of low-cost iron byproducts.

However, to provide an effective system for enhancing combustion in cyclone furnaces, there are several key steps in this process including:

- proper selection of candidate material,
- treatment of the dust to allow handling and shipping,

- design of equipment to blend the flux with the coal,
- design of a control system to adjust additive feed rate.

It is the use of these byproducts of steel and iron manufacturing to flux the ash and improve the cyclone operation that is new and unique.

Several candidate byproduct materials are available to provide a source of iron that can be technically acceptable, such as:

- Basic Oxygen Furnace (BOF) flue dust or precipitator fines.
- Blast Furnace flue dust
- Electric Arc Furnace dust
- Mill Scale fines

The materials are generally more than 50% iron by weight and are dusty or powdered. The preferred embodiment of this invention uses iron-bearing waste products containing more than 80% iron. Also, sludges containing iron plus oils and greases produced during metal finishing operations are suitable. These materials have the advantage of preventing fugitive emissions during handling and shipping. In addition, combustion of the oil or grease is also of value to boiler operators by replacing the heat input requirement from the coal and thus reducing fuel costs for producing electricity. An additional source of iron-bearing material is red mud from the bauxite mining industry.

The most favorable material was found to be flue dust and electrostatic precipitator dust from blast furnaces or BOFs. These are very fine dusts collected from iron or steel making furnaces. The material contains primarily Oxides of Iron and other metals in small amounts.

The elemental analysis of BOF flue dust was used to model its effect on PRB coal ash viscosity and the subsequent effect on the cyclone slag layer. The slag viscosity model showed that the BOF flue dust, when added to the coal to increase the ash iron percentage to 30% by weight, increased the thickness of the sticky layer in the cyclone by about 60%. The model also showed that the temperature at which the ash would have a viscosity of 250 poise would be reduced by at least 100°F. This temperature is an important indicator of the minimum

temperature at which the slag will flow. If the temperature at which the ash has a viscosity of 250 poise or lower is too high, then the slag will not flow to the slag tap on the floor of the boiler and will build up inside the boiler casing. This has been a problem on cyclone furnaces burning western coal at less than full design output.

Further, experience has shown that the presence of iron in the calcium aluminosilicate slags causes crystal formation in the melt when a critical temperature (T_c) is reached. These crystals change the flow characteristics of the slag causing it to thicken before it can flow. This phenomenon is known as "yield stress" and is familiar to those skilled in the art of non-Newtonian flow. Thicker slag allows the slag to capture and hold more coal particles. Therefore, much fewer coal particles escape the combustor without being burned.

To ADA-ES's knowledge, the alternatives when burning Powder River Basin coal in cyclone furnaces are to blend other more expensive coals which have high iron, or to add iron pellets to the coal. High iron coals always have high sulfur because the predominant form of iron in coal is iron sulfide (pyrite). Therefore, coal blending is prohibited by law due to increased sulfur emissions. A third alternative is to grind the coal going into the cyclone furnace much finer in order to increase the percentage of combustion that occurs for coal particles in flight. This option requires expensive modifications or replacement of grinding equipment, but moreover, it is counter to the original design and intent of the cyclone furnace and seldom solves the problem. All of these alternatives are much more expensive than the use of this byproduct material. Also, the smaller particle size of the iron byproduct material is better than larger forms of iron because the surface area of the fluxing material in contact with the slag drives the speed of a fluxing reaction. Therefore, the larger surface area of the dust compared to 1/4-inch pellets promotes fast and efficient fluxing.

Because of the small size of much of the available byproduct material, it can result in high fugitive dust emissions during handling and transportation. Therefore, a key step in this invention is to treat the material to provide acceptable dusting characteristics. The treatment can take place at the source of the material, at a transportation terminal, or at the plant site. There are several different types of treatment including:

- Adding water to the material. Laboratory tests have confirmed that the BOF dust is hydrophilic and mixes well with water. Adding water to the material forms a cohesive layer on the wetted surface after drying, which will eliminate fugitive emissions from the pile.
- The hydrophilic nature of the iron materials also means that they can be mixed as a slurry and made into any form desirable for shipping. Briquettes of the material can be made to decrease dust emissions during handling.
- Chemicals can be added to the slurried material to increase the cohesiveness of the final material. Laboratory tests have shown that xantham gum and phosphoric acid lead to very cohesive products.
- Spraying with conventional dust suppression chemicals such as calcium lignosulfonate can treat the material to prevent handling problems. This material is commonly used to reduce coal dust emissions, and can be applied at a range of concentrations from 1% to 10% at a cost of \$0.40 to \$4.00 per ton.

The byproduct iron material must be shipped from the source to the power plant. Shipping the material from the source to the furnace will be the most expensive part of the process. The material can be shipped by truck, rail, or barge. It is important to minimize the distance being shipped and the number of transfers.

The next step in the process is mixing the material with the coal and feeding to the furnace. The iron fluxing material can be added at a variety of locations including:

- Mixing with the coal at a shipping terminal
- Adding to the coal reclaim belt
- Adding to the coal bunkers
- Using an eductor to aspirate the material and add to the coal or primary air streams.

The final step in the process is to control the feedrate of the material. This can involve either feed forward or feedback control. The feed forward control would be based upon the chemical analysis of the coal being feed from the boiler. Feedback control could come from a variety of measured characteristics of boiler operation and downstream components such as:

- LOI as measured by on-line furnace analyzer
- Carbon content in ash as determined from ash samples extracted from the flue gas or precipitator hopper.
- Furnace exit gas temperature, which will decrease with less coal carryover from the cyclones.
- Slag optical characteristics such as emissivity or surface temperature.
- Slag tap flow monitoring.
- Stack opacity.

The preferred feed system for cyclone boilers is shown on Exhibit A (see KCBPU Proposal). The fluxing agent is transported pneumatically from covered railcar or truck to a storage silo where it is disengaged from the transport air by a bin vent filter. Level indicators in the silo show when the silo is full or nearing empty. The fluxing agent is discharged from the storage silo to a weigh feed bin through a rotary valve to the coal line. The mixture of coal, fluxing agent, and conveying air are then carried to the cyclone burner.

In order to complete our patent application and maintain our filing date we need to update our provisional patent application. The following items have been discovered in the course of our research in the past year and should be included in the filing. Please feel free to edit, add or subtract from these points as you see fit:

- The current embodiment of ADA-249 contains 2-8% zinc. Zinc is a known mineralizer in the cement industry. Mineralizers are substances that reduce the temperature at which the cement clinker sinters by providing more contact points for mass transfer. As such, mineralizers could enhance the rate at which iron fluxes with PRB coal ash. A range of 0.5-15% zinc is preferred in this application. A range of 2-8% is more preferred.
- The dusty, powdered iron material that is described in the patent application is extremely cohesive, and thus has a tendency to form dense, hard deposits in the delivery system. A number of flow aids and abrasive materials can be added to the material to aid in its handling. Possible flow aids include less than 5% of: ethylene glycol, proprietary agents known as "grind aids", and any other substance intended to reduce particle to particle attraction or sticking through electrostatic or mechanical means. Also included are any of a number of abrasive agents in the amount of 2-20% by weight. These agents include sand, blasting grit and boiler slag.
- Results of testing to date:
 - ADA-249 fed at about 20 lb/t coal allows slag to flow at lower temperatures. As a result, the boiler is able to operate overnight at lower load (60 MW without ADA-249, 35 MW with it) without freezing the slag tap and risking a boiler shutdown. The advantage is that the boiler can be operated at lower load (and more efficient units can operate at higher load) when the price of electricity is below the marginal cost of generating the electricity, thus saving on fuel costs. A rough estimate of the cost savings for KCBPU is about \$200K/y.
 - ADA-249 allows the cyclone boiler combustion process to operate more efficiently. These boilers are designed to burn the coal in a slag layer coating the cyclone barrel. When burning PRB coal, this slag layer is generally too thin and watery to capture the majority of the coal. Thus the coal burns in flight. This causes an increase in unburned coal and a decrease in boiler efficiency. To counteract this effect, additional air is supplied to the boiler and the coal is crushed more finely. This further decreases the boiler efficiency and increases the auxiliary power required to operate the boiler. Video recordings have shown that, with the additive, less unburned coal blows through the cyclone, which implies that the combustion process is operating closer to the way cyclones were designed to run.

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Exhibit A

Base System Layout

